Simple Liquid Phase Exfoliation of Molybdenum Trioxide (MoO3) rods into Nanosheets and Nanotubes

Bellare, P.[1] and Ravishankar, N.[1]

[1] Indian Institute of Science, India

Two dimensional(2D) nano-materials are interesting due their distinct properties like high specific surface area which make them suitable for catalytic and many other applications. One of the well-known layered oxides, MoO_3 exists in stable orthorhombic α-MoO_3 structure which involves stacking of MoO_6 octahedra bilayers along the [010] direction.[1] Electronic and optical properties of layered MoO_3 can be tuned via ion or molecule intercalation between the layers, followed by exfoliation to form 2D nanosheets. A simple room temperature method for the exfoliation of MoO_3 is developed, which involves the intercalation of oleylamine. Starting from MoO_3 rods, different systems and morphologies like $MoO_{(3-x)}$ - Oleylamine hybrid, $MoO_{(3-x)}$ nanosheets and $MoO_{(3-x)}$ nanotubes are produced. Orthorhombic *Φ#177;*-MoO_3 rods are synthesized by the hydrothermal method as already reported.[2] 2D-MoO_3 layers were realized via liquid phase exfoliation of Oleylamine intercalated $MoO_{(3-x)}$ hybrid. Completely exfoliated sheets roll up to form nanotubes upon removal of Oleylamine. Transmission Electron Microscope is extensively used to understand the morphology and structure of initial rods, the intermediate stages of intercalation, hybrid structure, completely exfoliated MoO_3 sheets and tubes. Structural and compositional information are also obtained using Scanning Electron Microscopy, X-ray photoelectron spectroscopy, Raman spectroscopy and X-Ray Diffraction. The intercalation of Oleyamine into the Van der Waals gap of MoO_3 rods results in the reduction of Mo to +5 state and creation of oxygen vacancies to produce $MoO_{(3-x)}$ - amine hybrid. The resulting sheets and tubes are also of non-stoichiometric, amorphous $MoO_{(3-x)}$. The amorphous $MoO_{(3-x)}$ sheets and tubes are heated in situ in Transmission Electron Microscope and ex situ in a furnace in both oxygen and inert atmosphere. $MoO_{(3-x)}$ recrystallizes to form orthorhombic, stoichiometric MoO_3 at around 500°C in oxygen atmosphere. Electrochromic properties of amorphous $MoO_{(3-x)}$ - oleylamine hybrids were studied. Furthermore, Au/MoO_3 hybrids are obtained via the wet-chemical growth of ultrathin Au nanowires on the exfoliated sheets. We have also investigated the electro-catalytic properties of the synthesized heterostructure.

We attempted to convert the MoO_3 rods into MoS_2, a widely used catalytic material, by a comparatively low temperature method. Transmission Electron Microscopy study shows that the MoS_2 spheres formed comprises of 4-8 ultrathin nanosheet stacked together. Since they contain a lot of exposed edges which are active towards catalysis, this material can act as a very good candidate as an electro-catalyst for H_2 evolution reaction.

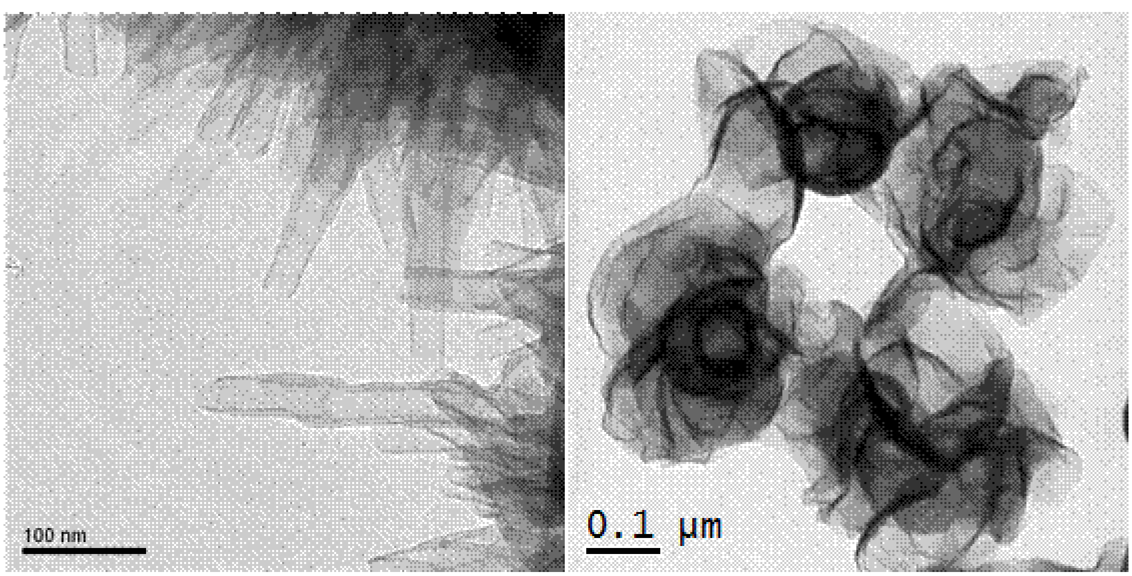

Figure: Transmission Electron Micrographs of (a)$MoO_{(3-x)}$ nanotubes and (b)MoS_2 nanosheets

Acknowledgement:

The authors acknowledge Department of Science and Technology, India for funding and AFMM and MNCF for microscopy facilities.

References:

1. Sreedhara, M.; Matte, H.; Govindaraj, A.; Rao, C., Synthesis, characterization, and properties of few-layer MoO_3. *Chem. Asian J* 2013, *8*, 2430.
2. Chen, J. S.; Cheah, Y. L.; Madhavi, S.; Lou, X. W., Fast synthesis of Φ#177;-MoO_3 nanorods with controlled aspect ratios and their enhanced lithium storage capabilities. *The Journal of Physical Chemistry C* 2010, *114* (18), 8675-8678.